“Energy Storage and Electrocatalysis Applications of Antimony-based Nanostructures”

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1. Introduction

With the ever-increasing adaption of large-scale energy storage systems and electric devices, the energy storage capability of batteries and supercapacitors has faced increased demand and challenges. The electrodes of these devices have experienced radical change with the introduction of novel nano-scale materials. As new generation heterostructure materials have attracted increasing attention due to their unique interfaces, robust architectures, and synergistic effects, and thus, the ability to enhance the energy/power outputs as well as the lifespan of batteries [1,2]. In the past decades, energy generation, storage and generation-storage integrated devices have drawn widespread attention in diverse fields including hybrid electric vehicles and smart portable electronics. By taking advantage of two different electrode materials, adding transition metal oxides, forming heterojunctions and mixing different types of electrode materials as composites, asymmetric supercapacitors (ASCs) can extend their operating voltage window and display more excellent energy-storage capacity than those of pristine as well as symmetric supercapacitors. Recent developments demonstrated that transition metal chalcogenides/oxides/halides have emerged as a promising class of materials for ASCs due to their low cost, fascinating redox reversibility and electronic conductivity [3].

Among known metal oxides, Sb_2O_3 is found in a variety of compositions and polymorphs that are having semiconducting properties which basically exists in two crystallographic structures: cubic (senarmontite) and orthorhombic (valentine). These structures are chemically stable at temperatures below 35 ◦C. The Sb_4O_6 consists of cubic Sb_2O_3, which can exist as individual molecules in the gaseous phase. Conversely, the orthorhombic Sb_2O_3 has a layered structure with elongated chains. Each chain is made up of three O_2 ions and four Sb^{3+}

ions, which are connected by weak Sb-O interactions. From an industrial perspective, it has a wide range of applications including flame retardants, semiconductors, sensors, catalysis, antifriction alloys, glass components, small arms, cable sheathing, and tracer bullets [4].

Electrochemical Supercapacitor

Supercapacitors (SCs) are a highly recommended power source for new applications since they store energy electrostatically rather than producing it from chemical reactions. In particular, anionic conducting materials brought to SCs the possibility of high-power density and excellent cycling stability. Further improvements to increase energy density and reduce costs rely heavily on increasing the capacitance of the porous material. The material can be used to make electrochemical energy storage devices with two electrodes (an anode and a cathode) of different materials. A piece of nickel foam coated with a particular number of as-synthesized products serves as the working electrode, with a Hg/HgO electrode serving as the reference electrode and a Pt electrode serving as the counter electrode. The use of carbon foam as the negative electrode (negatrode) and a metal oxide as the positive electrode (positrode) in electrochemical asymmetric supercapacitors (ASCs) has recently peaked[5].

Electrochemical Hydrogen Evolution

The development of sustainable clean energy captures great attention of scientists in recent years due to the ever-increasing environmental pollution and need of substantial energy. Molecular hydrogen (H_2) is considered as a promising candidate to meet global terawatt energy requirement in the future. Catalysis is the process of increasing the rate of a chemical reaction by adding a substance known as a catalyst which is not consumed in the catalysed reaction and can continue to act repeatedly. Because of this only very small amounts of catalyst are required to alter the reaction rate in principle[6]. The production of most industrially important chemicals involves catalysis. Similarly, most biochemically significant

processes are catalysed. Research into catalysis is a major field in applied science and involves many areas of chemistry and physics, notably organometallic chemistry and the materials science. Catalysis is relevant to many aspects of environmental science [7]. Three principle steps typically occur to convert H^+ to H_2 and to realize the hydrogen evolution reaction (HER), ($2H^+ + 2e^- \rightarrow H_2$) process in acidic media that including the adsorption of protons, electrochemical reduction, and desorption of hydrogen gas [8,9]. Therefore, efficient and durable electrocatalysts are required to minimize the over potential and to reduce the free energy barriers (i.e., ΔGH) of adsorbed hydrogen species, which make the HER process more prone to proceed efficiently in both thermodynamics and kinetics. In general, chemical reactions occur faster in the presence of a catalyst because the catalyst provides an alternative reaction pathway with lower activation energy than the non-catalysed mechanism. In catalysed mechanisms, the catalyst usually reacts to form a temporary intermediate, which regenerates the original catalyst in a cyclic process. A substance which provides a mechanism with higher activation energy does not decrease the rate because the reaction can still occur by the non-catalysed route. The added substance which does reduce the reaction rate is not considered a catalyst but a reaction inhibitor. Catalysts may be classified as either homogeneous or heterogeneous. A homogeneous catalyst is one whose molecules are dispersed in the same phase (usually gaseous or liquid) as the reactant's molecules. A heterogeneous catalyst is one whose molecules are not in the same phase as the reactants, which are typically gases or liquids that are adsorbed into the surface of the solid catalyst. Enzymes and other biocatalysts are often considered as a third category [10].

Literature review

Hai *et al.,* fabricated electrodes by combining Sb_2O_3 with multiwall carbon nanotubes for electrochemical detection of cadmium and lead ions. Furthermore, the presence of Sb_2O_3 in lead alloy batteries enhanced strength and mechanical durability. In the past, due to their

substantial theoretical capacity and excellent reversibility, antimony compounds have widely been employed in sodium-ion batteries [11]. Li *et al.* synthesized the anode for a sodium-ion battery by combining Sb2O3 and reduced graphene oxide, resulting in a high capacity of 584 mAh/g [12]. Xiao *et al.*, created an antimony@graphene oxide (GO) anode that surpasses all previously documented antimony anodes. The anode has a charge capacity of 340 mAh g^{-1} and showed exceptional durability when exposed to a current density of 250 mA per gram after completing 50 cycles of lithiation [13]. Xiao et al., reported photoelectrochemical properties of TiO_2/Sb_2S_3 heterojunction with CuO nanostructure as photocathode where charge transfer rate in device with CuO photocathode significantly enhanced [14]. Adimule et al. reported synthesis of hierarchical structured Gd-doped α-Sb_2O_4 as an advanced nanomaterial for high performance energy storage devices. Bimetallic oxide nanostructures of Gdx; Sb_2O_4 (x = 5, 8, 10 wt. %) appeared as a novel electrode material for batteries, according to this study, since they have a high specific capacity and cyclic stability. The specific capacitance of Gd; Sb_2O_4 NS (10 wt. percent) in 6 M KOH aqueous solution was 958 mAh/g at a current density of 0.15 A/g, with a capacitance retention rate of 86.5 % after 1000 cycles. This study presented a simple approach for synthesising Gdx; Sb_2O_4 NS for high-performance super capacitor applications[15].

Sharma and Basu fabricated centimetre-size Sb_2S_3/SiO_2 monolithic mimosa pudica nanoflowers for remediation of hazardous pollutants from industrial wastewater. Here, ‘mimosa pudica’ flower-like Sb_2S_3/SiO_2 monoliths were prepared by impregnation of antimony chloride solution in silica monoliths followed by treatment with potassium thiocyanate, refluxing and air calcination. The nanoflower-like morphology of the synthesized monoliths was verified using field emission scanning electron microscope images. The purity/crystallinity and the elemental state of the sulphide were confirmed using X-ray diffraction analysis and X-ray photon spectroscopy whereas energy dispersive

spectroscopy verified the homogeneous elemental distribution of the catalyst. The diffuse reflectance spectroscopy and photoluminescence spectroscopy confirmed that Sb_2S_3/SiO_2 monoliths had a narrow band gap (~1.57 eV) and low recombination rate of photoinduced charge carriers. Thermal stability of the materials was also investigated by thermogravimetric analysis [16]. Dai *Set al*. designed strategies in metal chalcogenide anode materials for developing high-performing sodium-ion battery. Generally, the common and effective methods include architecture design at nanoscale, compound with carbon materials, rational and unique array structure, the control of cut-off voltage and heteroatom doping [17].

Methodology

Hydrothermal method

It is important branches of inorganic synthesis. Hydrothermal technique is not just confined to the syntheses and growth of conventional and advanced materials but also take a very broad shape, covering several interdisciplinary branches of science and widely applied. Hydrothermal synthesis is a unique method for obtaining various nanostructures at ambient temperature and high vapour pressure in aqueous solution, which is also termed "hydrothermal method.'' The term "hydrothermal" has geologic origin. Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave in which a nutrient is supplied along with water. A temperature gradient is maintained between the opposite ends of the growth chamber. At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal [17].

Chemical bath deposition

Chemical bath deposition is a low-cost, low-temperature method for producing large-area semiconductor thin films (at temperatures ranging from 25 to 90 ^{o}C). For the deposition of different nanometal chalcogenide/oxide/hydroxide thin films, chemical bath deposition is routinely utilized. The regulated precipitation of the chemicals from the solution results in excellent deposits on appropriate surfaces. It does not require high-voltage equipment, can operate at room-temperature (between 30 and 100 degrees Celsius), and is thus affordable. Only an aqueous solution containing a few common chemicals and a substrate for the film to be deposited are required for this deposition method. Transition metal oxide films can be created by optimising CBD preparative factors such as deposition temperature, duration, pH, complexing agent, and so on. Various complexing techniques were used to deposit metal oxide films from a solution containing precursor [18].

SILAR Method

The successive ionic layer adsorption and reaction (SILAR) approach is a simple, less expensive, and faster method for the deposition of binary semiconducting thin films. It can also be used for large-area thin film deposition. The process was used to grow a variety of II–VI compounds, including CdS, ZnS, and CdS/ZnS multilayers. The substrate is submerged separately in two precursor solutions and rinsed in between with water to remove loosely bound species in the SILAR process. One SILAR cycle consists of cation precursor adsorption, water rinsing, anion precursor adsorption, reaction, and another rinsing. The thin film's growth, on the other hand, can be precisely regulated to within one SILAR cycle [19].

Physical, chemical and electrochemical measurements

X-ray Diffraction patterns will be used to differentiate the nature of crystalline materials from nanocrystalline materials [18]. The scanning electron microscope is important types of characterization technique and it uses a focused electron beam to scan solid sample from the

optical to the nanoscale range. In these types of characterization techniques, secondary electrons are emitted from the sample and it collected to create an area map of the secondary emission. The scanning electron microscopes will be used to determine the external morphology (texture), chemical composition, and crystalline structure of the nonmaterial samples [19]. Raman spectroscopy uses scattering of laser light to probe molecular structure. Of every million photons scattered, a single photon will interact with the vibrational states of a sample molecule and emit light of a different wavelength. **T**ransmission electron microscopy measurement provides the two-dimensional image and also it offers 50 million magnifications. Its resolution is 0.5Å in which the beam of electron is transmitted through ultrathin specimen and it interact with the specimen as it passes and gives an image. This technique is used to determine the particle size of nanoparticles [5].

Cyclic-Voltammetry (CV) is an electrochemical technique which measures the current that develops in an electrochemical cell under conditions where voltage is in excess of that predicted by the Nernst equation. This can be used to study qualitative information about electrochemical processes under various conditions, such as the presence of intermediates in oxidation-reduction reactions, the reversibility of a reaction [6]. Electrochemical impedance spectroscopy (EIS) **i**s an electrochemical technique to measure the impedance of a system in dependence of the AC potentials frequency. As well as is a powerful tool to study chemical and physical processes in solutions as well as in solids. Galvanostatic charge–discharge (GCD) curve is another intuitionistic approach to obtain specific capacitance. The GCD curves were performed at different current densities. Electrochemical hydrogen evolution reaction (HER) offers the polarization curves under the condition of different sweeping potential. The chronoamperometry j–t curve will be measured in a constant voltage. Oxygen evolution reaction (OER) is a limiting reaction in the process of generating molecular oxygen through chemical reaction, such as the oxidation of water during oxygenic photosynthesis,

electrolysis of water into oxygen and hydrogen. Developing improved catalysts for the OER is the key to the advancement of a number of renewable energy technologies, involving solar fuels production and metal–air batteries.

Problem undertaken

The wide applications of nanostructured are based on the progress in the synthesis of new nanostructured materials of different sizes and new morphologies. Therefore, further development in new materials having high energy storage performance and low overpotential for hydrogen production is essentially required. The best materials that can be used as an electrode in energy storage and electrocalysis can be Sb-based nanomaterials due to their wide potential window, highly redox reactions, distinct oxidation states, high conductivity, remarkably low overpotential, good thermal stability, long cycle life, and high rate capability as well as an environment friendliness.

Objectives

The focus of present work is to

(1) synthesize and characterize Sb_2O_3 based nanostructures.

(2) efforts will be made to convert Sb_2O_3 into Sb-chalcogenide/halide nanostructures using ion exchange method.

(3) investigate the influence of changes in the structure, surface area morphology on the electrochemical and electrocatalysis properties of the pristine and ionically converted Sb-based nanostructures.

(4) efforts will made to theoretically understand effect of changes in the physical and chemical properties the pristine and ionically converted Sb-based nanostructures.

(5) support experimental claims, various parameters like power density, energy density, specific capacitance, overpotential, etc., will be estimated for the pristine and ionically converted Sb-based nanostructures.

(6) develop Sb-nanostructures through ionically into metal chalcogenides/halides which will be envisaged in making energy storage and electro-catalysis devices for real ground applications will be explored.

(7) summarize and compare with previously reported Sb-based electrodes/catalysers for knowing suitability of the as-synthesized materials in energy storage and electrocatalysis technologies.

(8) Manuscript will be published in highly reputed/indexed journals.

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